Application Note 64

Low Background Solid Phase Extraction and Capillary GC Analysis of Chlorinated Pesticides

Solid phase extraction has been the main focus for sample preparation for monitoring semivolatiles, including pesticides, in aqueous hazardous waste samples because it provides rapid, on-site sample preparation and analysis. Supelco's ENVI-8 polymerically bonded octylsilane-silica packing provides good performance for solid phase extraction of pesticides from aqueous samples.

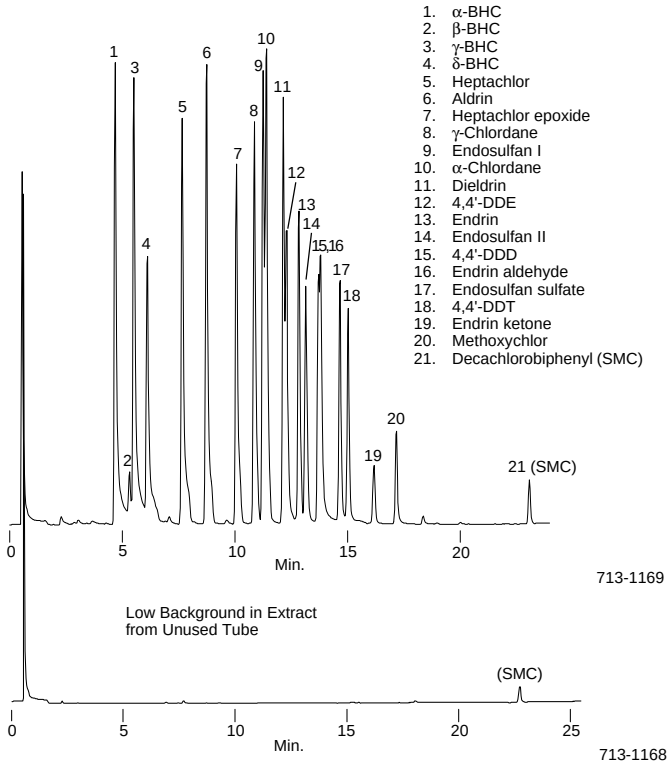
Key Words:

- chlorinated pesticides • solid phase extraction
- aqueous hazardous waste • ENVI-8 silica packing

Figure A. Extracted Pesticides

(Low Concentration, 10ng each/100mL sample)

Column: **PTE-5 QTM , 15m x 0.53mm ID, 0.5µm film**
Cat. No.: **25355**
Col. Temp.: 150°C (0.5 min) to 275°C at 5°C/min, hold 5 min
Det.: ECD
Inj.: extract obtained from procedure in Table 1, split/splitless injection, 45 sec hold, 200°C



Since the early 1980s, the US Environmental Protection Agency's Office of Solid Waste has been formulating new methods for identifying potentially hazardous abandoned waste sites. Currently, the EPA is developing a series of "quick turnaround" (QTM) methods, intended for use as screening methods, to allow decisions to be made quickly about the extent and nature of contamination at a site.

In EPA investigations, an octylsilane-modified, silica-based packing material has shown promise for solid phase extraction (SPE) of pesticides. We have developed a polymerically bonded octylsilane-silica packing, ENVI™-8, which performs well for extracting pesticides from aqueous samples. The polymeric bonding allows the material to resist pH extremes that might be encountered in sampling, and the high carbon loading should enhance the packing's capacity for nonpolar analytes. Extractions performed in our laboratories will be described here.

Any screening method for pesticides will require an extremely inert sample preparation system, because these analytes are of concern at very low concentrations – 10-250ng/100mL – and are monitored by GC with electron capture detection. To ensure reliable extractions, we used ENVI-8 packing in glass tubes with Teflon® frits. Extractions were performed using a Visiprep™ DL Solid Phase Extraction Vacuum Manifold■ (fitted with disposable Teflon sample guides) and a Visidry™ Drying Attachment▲. The samples were introduced directly into the tubes using custom glass tube adapters and the Visiprep large volume sampler.

Table 1. Solid Phase Extraction of Chlorinated Pesticides from Aqueous Hazardous Wastes

Extraction Tube:	0.5g ENVI-8 packing in 6mL glass tube, Teflon frits
Conditioning:	3mL methanol 2mL 5% methanol in water
Sample:	100mL aqueous sample, pH adjusted to 5.0-7.0
Addition:	add 5mL methanol add 10µL of 5.0µg/mL decachlorobiphenyl in methanol (SMC) introduce using Visiprep large volume sampler pass through SPE tube at 5mL/min.
Drying:	dry tubes under nitrogen flow for 2-3 minutes, using Visidry Drying Attachment
Elution:	add 5mL hexane:acetone (90:10), allow to soak into packing bed allow 2 minutes static extraction (no vacuum) add 5mL hexane:acetone (90:10), begin dropwise elution (low vacuum) reduce sample volume to 1mL, using nitrogen

Table 2. High Recovery of Pesticides by Solid Phase Extraction

	SPE Packing Capacity Level (250ng each pesticide)			Contamination Level (10ng each pesticide)		
Pesticide	% Recovery[a]	Std. Dev.[b]	Coef. Variat.	% Recovery[a]	Std. Dev.[b]	Coef. Variat.
α-BHC	91.4	7.0	7.7	84.6	9.2	10.9
β-BHC	100.1	10.1	10.1	—[c]	—	—
γ-BHC	94.0	6.1	6.4	88.2	10.8	12.2
δ-BHC	92.9	7.2	7.7	85.1	7.3	8.5
Heptachlor	95.0	5.7	6.0	86.6	6.4	7.3
Aldrin	94.9	4.8	5.1	84.7	13.9	16.4
Heptachlor epoxide	96.8	4.2	4.4	96.3	5.6	5.8
γ-Chlordane	97.4	4.5	4.6	85.8	6.3	7.3
Endosulfan I	94.6	4.7	4.9	84.8	8.5	10.1
α-Chlordane	96.4	4.6	4.7	90.2	7.4	8.2
Dieldrin	98.2	3.8	3.9	88.6	6.0	6.8
4,4'-DDE	99.9	4.2	4.2	80.1	7.7	9.6
Endrin	97.9	13.2	13.5	77.8	20.1	25.9
Endosulfan II	98.2	3.8	3.8	90.0	8.0	8.9
4,4'-DDD	104.4	5.4	5.2	98.6[d]	10.9	11.1
Endrin aldehyde	101.0	5.5	5.5	98.6[d]	10.9	11.1
Endosulfan sulfate	104.6	3.9	3.7	96.2	7.9	8.3
4,4'-DDT	107.9	4.9	4.5	95.3	13.4	14.1
Endrin ketone	110.4	14.3	12.9	104.6	29.9	28.6
Methoxychlor	108.4	3.2	2.9	93.4	13.1	14.0
Decachlorobiphenyl (SMC)	101.0	7.0	6.9	72.9	14.0	19.3

[a] Mean for 5 lots.
[b] n = 10 extractions.
[c] Could not be monitored under the GC conditions used (split-splitless, heated injection); cold on-column injection should reduce problem.
[d] Compounds coelute, area counts not separable at 10ng/mL each.

We packed 6mL glass tubes with 0.5g of ENVI-8 packing (retained with Teflon frits) and prepared pesticide standards for extraction, spiking the samples at 250ng each pesticide/100mL ("packing capacity level") and 10ng each pesticide/100mL ("contamination level"). The higher level would test whether the SPE tubes have adequate capacity for the analytes and the lower level would confirm that background levels are lower than the minimum detection levels for the analytes. After monitoring the effects of parameters such as pH and drying time on the extraction, we found the extraction procedure described in Table 1 to be excellent for this purpose.

Using the procedure in Table 1, we obtained high recovery levels for pesticides at both the high concentration and low concentration levels (Table 2). In general, recovery rates were very satisfactory, although they were somewhat variable for endrin and endrin ketone. Overall, the SPE tubes and the extraction procedure provided good results which met the criteria needed for pesticides extractions. Low contaminant level extractions exhibited few interferences, and lot-to-lot variability in recovery rates was acceptable.

If you are interested in examining the potential of these highly inert ENVI-8 solid phase extraction tubes for pesticides or other sample preparation procedures, please refer to our catalog or call our technical service chemists. You can also get information about other SPE tubes for environmental samples, and for descriptions of our SPE processing apparatus.

Ordering Information:

Description	Cat. No.
ENVI-8 SPE Tubes	
6mL glass tube, 0.5g packing, pk. of 30 Teflon frits	**57107**
Visiprep DL Disposable Liner SPE Vacuum Manifold	
12-port model	**57044**
24-port model	**57265**
Disposable Teflon Solvent Guides	
package of 100	**57059**
Visidry Drying Attachment	**57100-U**
Visiprep Large Volume Sampler	
for 4 samples	**57275**
Adapters	
for glass tubes	**custom**
PTE™-5 QTM Capillary Column	
15m x 0.53mm ID, 0.5µm phase film	**25355**

Trademarks
ENVI, PTE, Visidry, Visiprep – Sigma-Aldrich Co.
Teflon – E.I. du Pont de Nemours & Co., Inc.

For pesticide standards, refer to the Supelco general catalog.

■US Pat. Nos. D.289, 861; 4,810,471; other patents pending.
▲US Pat. No. 4,810,471; other patents pending.

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